

What Do We Know About Ethanol and Alkylates as Pollutants?

D.W. Rice, A.A. Marchetti, T. Buscheck, S.W. Layton

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What Do We Know About Ethanol and Alkylates As Pollutants?

David W. Rice*, Alfredo A. Marchetti*, Tim Buscheck**, and David W. Layton*

Background

Gov. Davis issued Executive Order D-5-99 in March 1999 calling for removal of methyl tertiary butyl ether (MTBE) from gasoline no later than December 31, 2002. The Executive Order required the California Air Board, State Water Resources Control Board (SWRCB) and Office of Environmental Health Hazard Assessment (OEHHA) to prepare an analysis of potential impacts and health risks that may be associated with the use of ethanol as a fuel oxygenate. The SWRCB contracted with the Lawrence Livermore National Laboratory (LLNL) to lead a team of researchers, including scientists from Clarkson University, University of Iowa, and University of California, Davis, in evaluating the potential ground and surface water impacts that may occur if ethanol is used to replace MTBE. These findings are reported in the document entitled *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate*. This document has been peer reviewed and presented to the California Environmental Policy Council and may be viewed at: <http://www-erd.llnl.gov/ethanol/>.

Ethanol used for fuels is made primarily from grains, but any feed stock containing sugar, starch, or cellulose can be fermented to ethanol. Ethanol contains 34.7% oxygen by weight. It is less dense than water, but infinitely soluble in water. Ethanol vapors are denser than air. One and a half gallons of ethanol have the same energy as one gallon of gasoline. Pure fuel ethanol, and gasoline with ethanol, conducts electricity, while gasoline without ethanol is an insulator. Corrosion and compatibility of materials is an issue with the storage of pure ethanol and gasoline with high percentages of ethanol, but these issues are less important if gasoline with less than 10% ethanol is used.

Methods

To evaluate potential ground and surface water impacts associated with the increased use of ethanol and alkylates in transportation fuels, the following steps were taken by a team of investigators at LLNL, University of Iowa, Clarkson University, and University of California, Davis:

- Began the development of a comprehensive life-cycle evaluation
- Performed literature reviews of environmental properties and transport and fate of ethanol, fuel alkylates, and benzene in the presence of ethanol.

* Lawrence Livermore National Laboratory

** Chevron Research and Technology Company

- Used screening models to evaluate ground and surface water impacts
- Evaluated chemical analysis techniques used to measure ethanol and alkylates in the environment.
- Submitted research findings to peer review.

As part of the overall assessment of ethanol as a fuel oxygenate, OEHHA has developed a draft Health Protective Concentration for ethanol in drinking water of 1100 mg/L. By comparison, the public health goal for MTBE is dramatically lower at 0.013 mg/L.

Impact of Gasoline Containing Ethanol on Surface and Ground Waters

As part of LLNL's effort, release scenarios were developed based on the production, distribution, and use of ethanol as a fuel oxygenate. To date, the following scenarios were evaluated because they were most likely to have impact: leaking under ground fuel tank releases, rail tank car release to a river, and bulk ethanol release at a fuel distribution terminal. Not all release scenarios were evaluated and a complete life cycle analysis needs to be performed.

Impact of Leaking Under Ground Fuel Tank Releases

Ethanol is degraded very rapidly in soils and water. Ethanol will most likely be preferentially utilized over all the BTEX compounds under aerobic and anaerobic conditions. The preferential degradation of ethanol in ground water may result in longer dissolved benzene plume lengths. Ethanol constitutes a significant demand on oxygen (and other electron acceptors) and is likely to cause the depletion of electron acceptors for BTEX degradation. This is particularly important for benzene because it degrades slowly under anaerobic conditions (Corseuil, et al., 1997; Alvarez and Hunt, 1999). Ethanol concentrations exceeding 40,000 mg/L in microcosm experiments were toxic to the microorganisms, as shown by a complete lack of oxygen consumption (Hunt et al., 1997).

Three independent screening model assessments indicate that average benzene plumes may increase 24 – 33 % in the presence of ethanol. In relatively rare cases, benzene plumes may increase as much as 100%. These models make two important simplifying and conservative assumptions: 1) benzene is not degraded in the zone where ethanol is being rapidly degraded, 2) the biodegradation rate for benzene is uniform over the length of the benzene plume. If these assumptions are not representative of actual processes, then benzene plume lengths may be shorter than estimated by the screening models (McNab et al., 1999).

The comparative potential impact of increased benzene plume lengths, relative to MTBE, were also evaluated. A baseline potential impact was developed for benzene without ethanol present. This baseline was used to compare the impacts of MTBE plumes and benzene plumes with ethanol present. Compared to the use of ethanol, the estimated potential future increase in public wells impacted by MTBE is significantly higher if MTBE were to remain the primary fuel oxygenate (Powers et al., 2001).

There have been concerns about ethanol increasing the ground water solubility of fuel hydrocarbon components, such as benzene. The impact of ethanol co-solubility effects on benzene dissolution will likely be very minor when 10% gasohol is used. The impacts of increased dissolution and mobility may be significant when bulk pure fuel ethanol is released on to fuel hydrocarbons already present in the subsurface. The co-solubility effects on less soluble gasoline components, such as alkylates, has not been evaluated.

Although gasoline containing 10% ethanol (gasohol) is widely used in Iowa and Nebraska, the ethanol concentrations associated with gasohol releases are typically not measured because ethanol is not a regulated pollutant. There is a perception that no important differences exist between gasoline with and without 10% ethanol, but potential differences have not been evaluated in the field. The lack of historical benzene and ethanol concentration data at gasohol leak sites is a major knowledge gap.

Impact of a Rail Car Release to Surface Waters

The impacts of ethanol-containing gasoline on surface water resources were also evaluated. The loss mechanisms for MTBE and ethanol from surface waters are different. Ethanol is removed through biodegradation, while MTBE is removed through volatilization at the water's surface. If there are spills of equal mass, MTBE will have much greater impact to surface water drinking supplies. Washout of ethanol from the atmosphere through rain may be 40 times greater than MTBE. Ethanol concentrations in rain could be about 40 to 65 ppb. Ethanol will be rapidly removed from rainwater through biodegradation.

Bulk ethanol release at a fuel distribution terminal

In March, 1999 a 19,000-gallon release of neat ethanol occurred from an above ground storage tank at a Northwest fuel distribution terminal. Following the ethanol release, a groundwater sampling program was implemented to delineate the ethanol plume and understand the impact of ethanol on the existing non-aqueous phase liquid (NAPL) and dissolved hydrocarbon plumes (Buscheck et al., 2001).

With a sufficiently large amount of ethanol in a localized subsurface environment, gasoline and water become completely miscible with each other and merge into a single phase (Powers et al., 2001). Laboratory experiments demonstrate a logarithmic increase in BTEX with increasing ethanol concentrations (Heerman and Powers, 1998). Neat ethanol releases could result in an order of magnitude increase in BTEX concentrations (Powers et al., 2001) (da Silva et al., 2001) conducted microcosm experiments to study aerobic, denitrifying, iron-reducing, sulfate-reducing, and methanogenic conditions. Aquifer materials from the Northwest Terminal were included in these experiments. Ethanol retarded toluene degradation under aerobic, sulfate-reducing, and iron-reducing conditions. Ethanol enhanced toluene degradation under denitrifying conditions.

Ethanol migrated approximately 250 feet between March and September 1999, consistent with groundwater velocity estimates, but was not detected at that distance after September 1999. Ethanol concentrations in two monitoring wells near the release have declined by a

factor of 50 to 150 over two years. Ethanol appears to enhance the thickness of NAPL in two monitoring wells. Co-solvent effects of ethanol are suggested by benzene concentrations increasing by a factor of 10 or more in one monitoring well. The presence of ethanol has created a strongly anaerobic groundwater system, demonstrated by low dissolved oxygen, depleted nitrate and sulfate, and high methane concentrations.

Increased Use of Alkylates in Gasoline

Alkylates are high-octane solutions of isoalkanes that are blending components of gasoline. Alkylates are branched hydrocarbons with octane ratings close to 100. With a phase out of MTBE, the alkylate composition of gasoline is expected to increase to maintain octane levels. Compared to MTBE, less ethanol is required to meet specified oxygen content in gasoline. Adding additional alkylates to gasoline that contains ethanol may compensate for this octane deficit.

Alkylates have low solubility in and are less dense than water. They are complex mixtures, and properties like biodegradability or toxicity are not easily extrapolated to all alkylate compounds. Cancer risk, reproductive and developmental effects have not been well studied.

Alkylates have high Henry's law constants. In air-water systems they concentrate mainly in the air phase. Air is the major sink for surface releases of alkylate with 2-3 days half-life due to hydroxy-radical oxidation. Alkylates are expected to have limited potential for rainout from the atmosphere. Alkylates have moderate ozone forming potential compared to other gasoline components. After a surface water spill, these compounds will rapidly volatilize from the surface film.

Primary subsurface transport will likely be in the vapor phase. During a subsurface release, depending on soil characteristics and source location, significant migration to the atmosphere is possible. There is also strong absorption of alkylates in the soil organic phase (high K_{ow}). Any persistence of alkylates in groundwater would probably be more of a taste and odor issue.

With the increased use of alkylates in gasoline, minor increases in alkylates probably will occur in the subsurface at release or spill sites. Alkylate solubility in water is very low (10^{-4} - 10^{-5} M). Persistence of isooctane and other branched alkanes in groundwater is poorly understood relative to BTEX compounds. Branched alkanes tend to be recalcitrant in the subsurface, but there have only been a few experimental biodegradation studies. A laboratory experiment conducted by Solano-Serena (1998) used an unpolluted forest soil to incubate a gasoline solution. After 28 days at 30°C, 20 % of the isooctane was degraded. Benzene, in contrast, was completely degraded. The corresponding degradation half-life is about 88 days for isooctane. Based on the results of a field study of a contaminated aquifer by Nielsen (1996), it is likely that the *in-situ* degradation of isooctane will be considerably longer and will depend in part on the occurrence of certain natural microorganisms capable of degrading fuel hydrocarbons.

The behavior of alkylates in the subsurface is less understood for a gasohol spill. Ethanol as a co-solvent can increase the solubility of alkylates; e.g., calculations show that for an ethanol concentration in water of 10% [v] the solubility of isooctane would increase by ~1.5.

Conclusions and Recommendations

The water resource impacts associated with the use of ethanol will likely be significantly less than those associated with the continued use of MTBE. The key factor is the biodegradability of ethanol compared to MTBE. If a decision is made to use ethanol as a fuel oxygenate, several additional analyses and experiments should be performed to help manage the use fuels containing ethanol (Rice et al., 1999).

- An expanded life cycle analysis of ethanol and alkylates is needed, including development of direct and indirect impacts of ethanol and alkylate production, distribution, and use.
- Field and laboratory studies should be performed to improve our understanding of:
 - the degradation of dissolved benzene by ethanol degrading microbial populations,
 - changes in benzene degradation rates over the length of a dissolved benzene plume,
 - vadose zone transport of gasoline components in the presence of ethanol, and
 - Henry's law constants for alkylates.
- Additional historical case data from 10% gasohol release sites should be collected and analyzed.
- Potential impacts associated with the increased use of alkylates in reformulated fuels needs to be evaluated further.

For more information, please contact: David W. Rice, Lawrence Livermore National Laboratory, PO Box 808, L-528, Livermore, California 94551. Phone: (925) 423-5059. Fax: (925) 422-2095. Email: rice4@llnl.gov.

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